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(54) Title: PROCESS FOR THE PREPARATION OF SOLUTIONS OF ANIONIC ORGANIC COMPOUNDS

(57) Abstract: A process for the preparation of concentrated solutions or suspensions of anionic organic compounds is described, which process comprises a) acidifying an aqueous solution or dispersion of an anionic organic compound that comprises salts and/or impurities, to a pH of 4.5 or less, if the pH is above that value, so that b) the anionic organic compound becomes insoluble in water and precipitates out in the form of the free acid, c) bringing the suspension, by means of micro- or ultra-filtration, to a salt content of less than 2 % by weight, based on the total weight of the retained material, with d) optional washing out of the salts with water at a pH of less than 4.5, e) then optionally washing with water until acid-free, then f) increasing the concentration so that the content of anionic organic compound is from 5 to 50 % by weight, and g) optionally dissolving the anionic organic compound by addition of a suitable base.

Process for the preparation of solutions of anionic organic compounds

The present invention relates to a process for the preparation of solutions of anionic organic compounds, to the solutions so prepared and to the use of such solutions. In this context, anionic organic compounds are understood to be, especially, dyes and fluorescent whitening agents and also intermediates for the preparation thereof.

In recent years, the use of concentrated aqueous solutions, for example of dyes and fluorescent whitening agents, has gained in importance, that being the case because of the advantages that such solutions have over the corresponding powder forms. The use of solutions avoids the difficulties associated with dust formation and frees the users from the time-consuming, and often difficult, task of dissolving the powder in water. The use of concentrated solutions has also been encouraged by the development of continuous processes for dyeing or whitening paper because it is advantageous in those processes for the solution to be introduced directly into the hollander or added at some other suitable point in paper manufacture.

In the case of a number of dyes and fluorescent whitening agents, however, formulating concentrated solutions presents difficulties because the concentrated solutions, especially when they still comprise significant amounts of inorganic salts, tend to gel. It is then not practically possible for such gels to be purified and/or desalted by filtering off and washing.

Furthermore, on storage, especially at temperatures below room temperature, there are often formed in the concentrated solutions deposits which either cannot be redissolved at all or can be redissolved only by carrying out additional work. Moreover, if concentrated anionic dye or fluorescent whitening agent solutions are to be suitable as commercial forms, they should, on being diluted to produce the dyebaths, yield clear solutions containing about from 1 to 3 % by weight of dye or fluorescent whitening agent without a precipitate, and that should also be the case over a pH range that is as wide as possible.

The present invention is based on the problem of providing suitable concentrated solutions of such dyes and fluorescent whitening agents and also intermediates for the preparation thereof in which the mentioned difficulties do not occur.

It has now been found that, by means of the process described hereinbelow, it is possible to prepare, simply and economically, concentrated solutions that excellently meet the demands made. The process represents a simple and economical method for converting anionic organic compounds present in a poorly soluble salt form into a readily soluble form by temporarily converting particular or all acid groups into the acid form and subsequently neutralising them using suitable bases.

The present invention accordingly relates to a process for the preparation of concentrated solutions or suspensions of anionic organic compounds, which process comprises

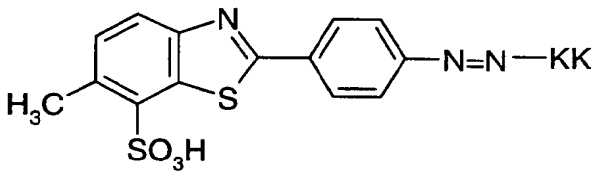
a) acidifying an aqueous solution or dispersion of an anionic organic compound that comprises salts and/or impurities, to a pH of 4.5 or less, if the pH is above that value, so that
b) the anionic organic compound becomes insoluble in water and precipitates out in the form of the free acid,
c) bringing the suspension, by means of micro- or ultra-filtration, to a salt content of less than 2 % by weight, based on the total weight of the retained material, with
d) optional washing out of the salts with water at a pH of less than 4.5,
e) then optionally washing with water until acid-free, then
f) increasing the concentration so that the content of anionic organic compound is from 5 to 50 % by weight, and
g) optionally dissolving the anionic organic compound by addition of a suitable base.

Anionic organic compounds are to be understood as being especially dyes and fluorescent whitening agents and intermediates for the preparation thereof.

Suitable dyes for the process according to the invention are anionic dyes that are stable and insoluble in water at pH values of less than 4.5. Such dyes may belong to any desired class. They are, for example, dyes containing at least one sulfonic acid group and/or carboxylic acid group from the following classes of dyes: metal-free or metal-containing mono-, bis- and poly-azo dyes, pyrazolone, thioxanthone, oxazine, stilbene, formazan, anthraquinone, nitro, methine, triphenylmethane, xanthone, naphthazarine, styryl, azastyryl, naphthoperinone, quinophthalone and phthalocyanine dyes. Such dyes may contain one or more fibre-reactive groups in the molecule.

Preference is given to azo dyes containing at least one sulfo group and, amongst those, especially the so-called azo direct dyes, for example those referred to in The Colour Index, Third Edition, Volume 2 (The Society of Dyers and Colourists, 1971). A further preferred class is that of the so-called stilbene dyes.

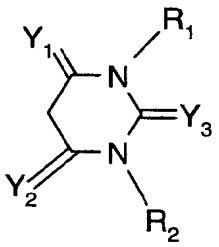
Special preference is given to dyes that are suitable for the dyeing of paper and, amongst those, especially the dyes of formula



(1)

wherein KK is the radical of a coupling component.

KK is preferably a coupling component of formula



(2)

wherein

Y_1 and Y_2 are each independently of the other =O, =NH or =N-C_1-C_4alkyl,

Y_3 is =O, =S, =NR or =N-CN, R being hydrogen or C_1-C_4alkyl, and

R_1 and R_2 are each independently of the other hydrogen, unsubstituted or substituted alkyl or unsubstituted or substituted phenyl.

In formula (2) above, only one tautomeric form is indicated for the coupling component, but the formula is intended also to encompass the other tautomeric forms.

When R_1 and/or R_2 is/are an unsubstituted or substituted alkyl group, it is to be understood as being, for example, methyl, ethyl, n- or iso-propyl, n-, sec- or tert-butyl, straight-chain or branched pentyl or hexyl or cyclohexyl; the said radicals may be mono- or poly-substituted, for example by OH, C_1-C_4alkoxy or by C_1-C_4hydroxyalkoxy.

Examples of suitable substituted alkyl radicals are: methoxymethyl, ethoxymethyl, ethoxyethyl, ethoxypropyl, n-propoxymethyl, butoxyethyl and 2-hydroxyethoxypentyl.

When R_1 or R_2 is unsubstituted or substituted phenyl, the latter may be mono- or poly-substituted, for example by C_1-C_4alkyl, C_1-C_4alkoxy, halogen, e.g. fluorine, chlorine or bromine, or by nitro.

R_1 and R_2 are preferably hydrogen or C_1-C_4alkyl.

Y_1 and Y_2 are preferably =O or =NH; furthermore, Y_1 and Y_2 are preferably the same.

Y_3 is preferably =O, =S, =NH or =N-CN, especially =NH.

The dyes of formula (1) are known or can be synthesised in a manner known *per se*.

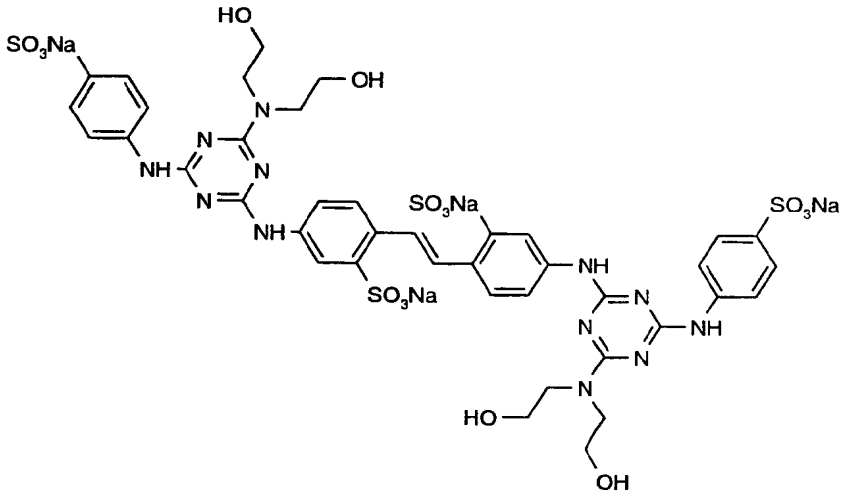
The stilbene dyes are complex dye mixtures which result from the condensation of 4-nitrotoluene-2-sulfonic acid with itself or with other aromatic compounds. Their structure is defined by the mode of preparation. Suitable stilbene dyes are, for example, those described in The Colour Index, Third Edition, Volume 4 (The Society of Dyers and Colourists, 1971) under the constitution numbers from 40.000 to 40.510.

Suitable dyes for the process according to the invention are preferably Direct Yellow 11 and its derivatives Direct Yellow 6 and Direct Orange 15, which derivatives are obtainable by means of reductive sub-steps additionally incorporated into the synthesis.

Suitable fluorescent whitening agents for the process according to the invention are sulfo- and/or carboxy-group-containing whitening agents of various classes, for example bis-(triazinylamino)stilbenes, bis(triazolyl)stilbenes, bis(styryl)biphenyls and bis(benzofuranyl)-

biphenyls, bis(benzoxalyl) derivatives, bis(benzimidazolyl) derivatives, coumarin derivatives and pyrazoline derivatives.

For example, the process according to the invention is suitable for the preparation of concentrated solutions of the following fluorescent whitening agents:



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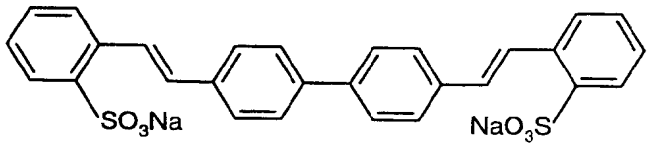

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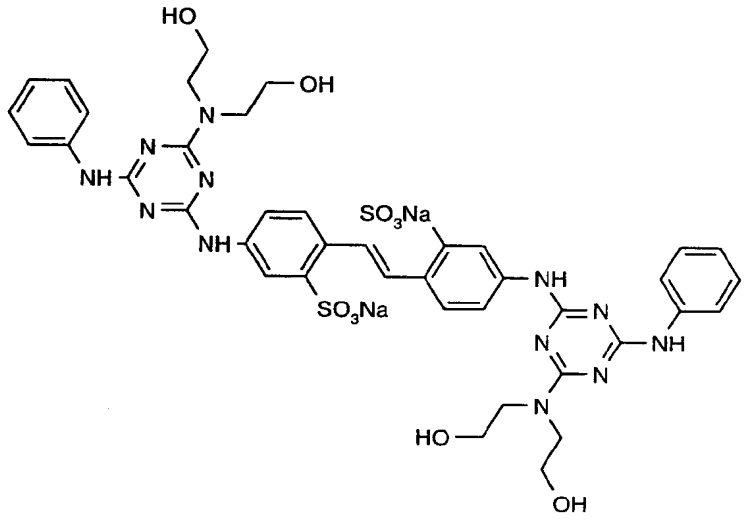

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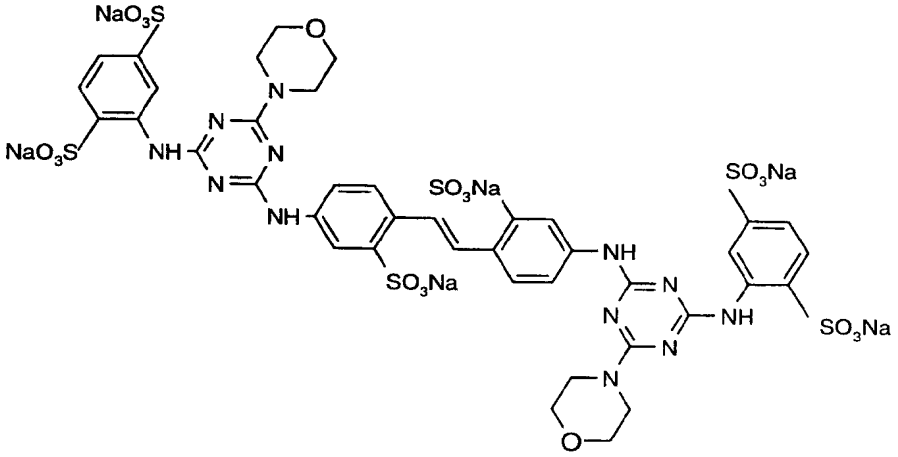

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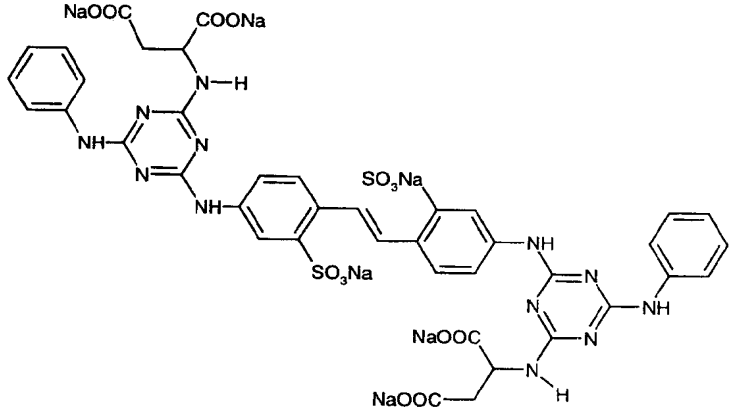
and



(7).

Suitable intermediates for the process according to the invention are especially anionic intermediates that are used for the synthesis of dyes or of fluorescent whitening agents.

They are, especially, aromatic sulfonic acids that also carry one or more further substituents, for example amino, nitro, alkyl or hydroxy.

Especially suitable intermediates are, for example, 2-amino-5-hydroxynaphthalene-7-sulfonic acid, 4-aminotoluene-2-sulfonic acid, dehydroparathiotoluidinesulfonic acid, 4,4'-diamino-stilbene-2,2'-disulfonic acid, 4,4'-dinitrostilbene-2,2'-disulfonic acid, 4,4'-diamino-diphenyl-amine-2-sulfonic acid and 4-nitrotoluene-2-sulfonic acid.

The process according to the invention is carried out in particular as follows:

The process usually starts from an aqueous synthesis solution or suspension that, besides the anionic organic compound, also comprises greater or lesser amounts of starting materials, secondary products, salts or other impurities. If, however, the anionic organic compound is present in solid form or in the form of a slurry or paste, it is first dispersed in water so that an aqueous suspension or solution is obtained.

If the anionic organic compound is already present therein in the form of the free acid, the micro- or ultra-filtration is carried out directly thereafter, whereas if it is present in salt form, the first step of the process according to the invention is to convert the salt into the free acid.

In the case of compounds containing a plurality of sulfo groups it is sometimes advantageous to carry out the conversion into the free acid in a plurality of steps at different pH values and/or temperatures or to convert only particular sulfo groups into the free acid.

For preparation of the free acid, an aqueous solution or dispersion of the anionic organic compound, which comprises salts and/or other impurities, is acidified to a pH of 4.5 or less and is stirred or mixed until the anionic organic compound has been virtually completely converted into the free acid and is therefore insoluble in water and precipitates out. That is carried out preferably by adding a strong inorganic acid, for example hydrochloric acid or sulfuric acid, until the desired pH has been obtained. The conversion is advantageously carried out at a temperature of from 15 to 140°C, especially from 20 to 95°C.

The optimum pH, the temperature, the concentration and the duration of mixing must be matched to the anionic organic compound and the desired degree of conversion. The optimum conditions can readily be determined by means of appropriate tests.

In the case of anionic organic compounds that are difficult to convert it can be useful first to subject the solution or suspension to partial desalting and only then to carry out conversion into the free acid. That can be done, for example, by means of nanofiltration or intermediate isolation of the anionic organic compound. In addition, special synthesis techniques for generating low-salt synthesis solutions can be used, for example simultaneous diazotisation and coupling. It is also possible to wash an anionic organic compound that has been only partially converted into the free acid, until it has a low salt content and then to add acid again and, optionally at elevated temperature, to carry out stirring or mixing.

Washing and conversion into the free acid can also be carried out in continuous succession by circulating the suspension through a micro- or ultra-filtration unit which is connected in series to a reactor for converting into the free acid and, optionally, heating.

In the process according to the invention microfiltration is preferably carried out. However, ultrafiltration can also be used. Because of the relatively fine membranes, the latter is suitable especially for compounds having an amorphous structure. However, the performance is often worse.

Micro- or ultra-filtration is carried out by generally known methods that are customary *per se* using known membranes. The membranes may consist of acid-resistant organic or inorganic material. Ceramic membranes are especially suitable - in the case of microfiltration especially those having a pore size of from 20 to 1000 nm, more especially from 100 to 800 nm, and in the case of ultrafiltration especially those having a pore size of from 1 to 20 nm.

The temperature during micro- or ultra-filtration is approximately at from room temperature to about 95°C, preferably from 50 to 85°C. The pressure is dependent, *inter alia*, on the nature of the membrane, but is usually from 1.5 to 10 bar, preferably from 3 to 6 bar.

Washing and increasing the concentration by means of micro- or ultra-filtration is carried out until the desired salt content and the desired concentration of anionic organic compound are obtained. Normally, a content of inorganic salts of less than 2 % by weight, preferably less than 0.5 % by weight, based on the total weight of the suspension, is sought.

The content of anionic organic compound after micro- or ultra-filtration is preferably from 5 to 50 % by weight, especially from 10 to 40 % by weight, based on the total weight of the suspension.

After micro- or ultra-filtration, any desired base can be added to the low-salt or salt-free suspension obtained, in order to obtain readily soluble salts of the anionic organic compounds with any desired cations. Suitable bases are, for example, LiOH, NH_4OH, or organic amines, e.g. a C_4-C_{12}trialkylamine, C_4-C_{12}dialkylamine, C_2-C_{15}alkanolamine or polyglycol amine. Preference is given to the use of LiOH, NH_4OH or an alkanolamine.

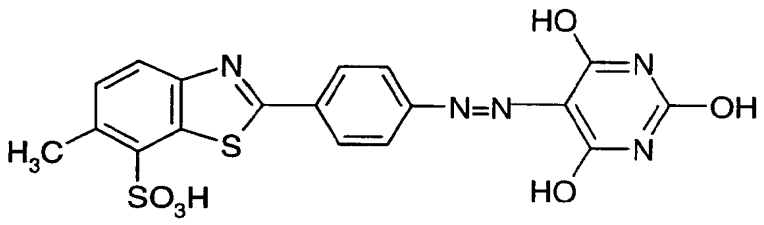
The solutions of dye or whitening agent obtained may be used directly in that form or optionally after dilution. They may also, however, in customary manner, be dried and used in the form of powders or granules.

In the following Examples, parts refer to parts by weight, unless otherwise indicated, and percentages relate to percent by weight. The temperatures are given in degrees Celsius.

Example 1: 96 parts of dehydrothio-p-toluidinesulfonic acid are dispersed in 600 parts of water at 60° and dissolved at pH 7.5 to 8 by adding 25 parts of 50 % sodium hydroxide solution. After dissolution is complete, 46.3 parts of sodium nitrite solution (46 parts in 100 parts of water) are added. The resulting solution is added over the course of 20 minutes to 90 parts of 32 % hydrochloric acid and a little ice, the temperature being maintained at from 15° to 20° by continuous addition of ice. Stirring is carried out for 30 minutes and about 1400 parts of a yellow suspension are obtained. Before coupling, any excess sodium nitrite is removed using sulfamic acid.

40.5 parts of barbituric acid are added to the resulting suspension and stirring is carried out for 15 minutes. Then about 46 parts of 50 % sodium hydroxide solution are added over 3 hours so that a pH of 3.3 is maintained. When no more sodium hydroxide solution is taken

up, the mixture is heated to 75° and, at that temperature, 69 parts of 32 % hydrochloric acid are added over 5 minutes; stirring is then carried out for a further 2 hours at from 80° to 85°, the orange suspension, which contains the sodium salt of the dye, being converted into the yellow suspension of the free acid of formula



(8).

The volume is about 1800 parts.

The suspension is cooled to from 50° to 60° and the volume is reduced by one third by micro- or ultra-filtration in a conventional micro- or ultra-filtration system equipped with membrane cartridges (ceramic membrane on Al_2O_3 carrier material, pore size from 100 to 800 nm).

Then, in the same system, washing is carried out firstly with 3600 parts of deionised water that has been adjusted to a pH of 1.0 using HCl and then with 2400 parts of deionised water that has been adjusted to a pH of 4.5 using HCl. The concentration is then increased to 900 parts by volume.

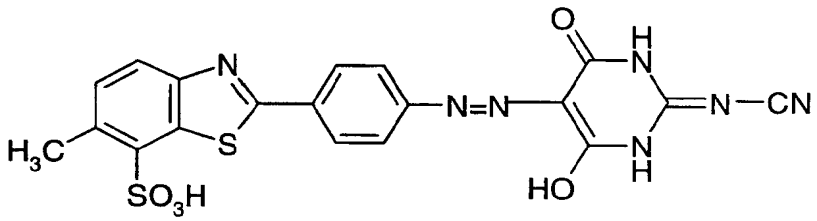
A solution of 6.5 parts of lithium hydroxide • 1 H_2O and 34 parts of triethanolamine in 80 parts of water is added to the resulting suspension. A clear dark solution having a pH of about 7 is obtained. After adding 80 parts of water, there are obtained 1100 parts of a storage-stable dye formulation having a sodium content of less than 300 ppm and a dye content of 11.6 % (calculated as free acid).

If micro- or ultra-filtration is not used in the procedure and the dye is isolated from the suspension of the free acid by filtering off and washing the filter cake with water, it is not possible in industrial practice to obtain the desired low sodium content by means of conventional filter presses.

Example 2: The procedure is as described in Example 1 but, instead of barbituric acid, an equivalent amount of cyanoiminobarbituric acid is used and the conversion into the free acid

is carried out at 85° using 10 % HCl. The concentration is then increased by a factor of 2 in the same microfiltration system. Washing is then carried out using 4 times the volume of deionised water adjusted to a pH of 3.0 using HCl.

After continuing to proceed as in Example 1, there is obtained, using triethanolamine alone as base, a storage-stable formulation of the dye of formula

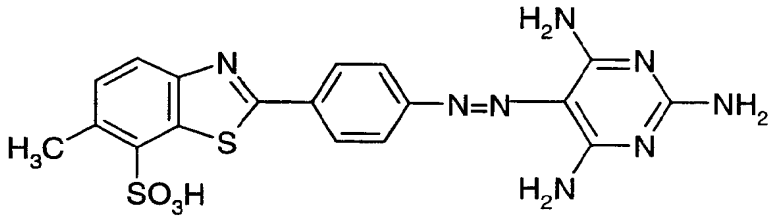


(9),

having a chloride content of less than 0.1 % and a sodium content of less than 0.05 %.

Example 3: The procedure is as described in Example 1 but, instead of barbituric acid, an equivalent amount of 2,4,6-triaminopyrimidine is used and the conversion into the free acid is carried out at 60° and at a pH of from 1 to 2. The concentration is then increased by a factor of 2 in the same microfiltration system. Washing is then carried out using 5 times the volume of deionised water adjusted to a pH of 1.0 using HCl.

After continuing to proceed as in Example 1, there is obtained a storage-stable formulation of the dye of formula



(10),

using as a mixture of bases an equivalent amount of a 1:1 mixture of 3-diethylamino-1-propylamine and diethanolamine.

Example 4: 800 parts of water are introduced into a flange flask and 120 parts of NaOH in solid form are so introduced therein that the temperature does not rise above 60°. 217 parts

of 4-nitrotoluene-2-sulfonic acid are then added to the warm sodium hydroxide solution over the course of 5 minutes. The temperature is then increased to 74° over the couse of 1 hour and 100 parts of water are then added dropwise over the course of a further hour. The pH of the reaction mixture is greater than 12. Stirring is carried out for a further 4 hours at from 70 to 75°, then 650 parts of water are added and, over the course of 25 minutes, concentrated sulfuric acid is added until the dye has completely precipitated out. The reaction mixture is then stirred for a further 30 minutes in the hot state.

In analogous manner to that described in Example 1, there is obtained by means of microfiltration, by acid washing with dilute sulfuric acid, a low-salt dye form which, after increasing the concentration and neutralising using diethanolamine, yields a stable liquid formulation of the dye Direct Yellow 11.

Examples 5 - 49: The following Table contains further dyes that can, in accordance with the procedure according to Examples 1 - 3, be made into storage-stable concentrated solutions by micro- or ultra-filtration. The dye names relate to The Colour Index, Third Edition, Volume 2 (The Society of Dyers and Colourists, 1971).

Example	Dye	Example	Dye
5	Direct Yellow 27	6	Direct Yellow 127
7	Direct Yellow 132	8	Direct Yellow 137
9	Direct Orange 15	10	Direct Yellow 142
11	Direct Yellow 4	12	Direct Yellow 148:1
13	Direct Yellow 153	14	Direct Yellow 157
15	Direct Yellow 6	16	Direct Yellow 169
17	Direct Orange 26	18	Direct Red 16
19	Direct Red 23	20	Direct Red 31
21	Direct Red 238	22	Direct Red 252
23	Direct Red 253	24	Direct Red 254
25	Direct Red 262	26	Direct Violet 9
27	Direct Violet 51	28	Direct Violet 66
29	Direct Violet 99	30	Direct Yellow 51
31	Direct Yellow 86	32	Direct Yellow 154

33	Direct Orange 118:1	34	Direct Red 80
35	Direct Red 239	36	Direct Violet 35
37	Direct Blue 67	38	Direct Blue 75
39	Direct Blue 78	40	Direct Blue 80
41	Direct Blue 218	42	Direct Blue 267
43	Direct Blue 273	44	Direct Blue 281
45	Direct Blue 290	46	Direct Blue 301
47	Direct Blue 86	48	Direct Blue 199
49	Direct Black 22	50	Direct Black 168
51	Direct Blue 86		

What is claimed is:

1. A process for the preparation of concentrated solutions or suspensions of anionic organic compounds, which process comprises

a) acidifying an aqueous solution or dispersion of an anionic organic compound that comprises salts and/or impurities, to a pH of 4.5 or less, if the pH is above that value, so that

b) the anionic organic compound becomes insoluble in water and precipitates out in the form of the free acid,

c) bringing the suspension, by means of micro- or ultra-filtration, to a salt content of less than 2 % by weight, based on the total weight of the retained material, with

d) optional washing out of the salts with water at a pH of less than 4.5,

e) then optionally washing with water until acid-free, then

f) increasing the concentration so that the content of anionic organic compound is from 5 to 50 % by weight, and

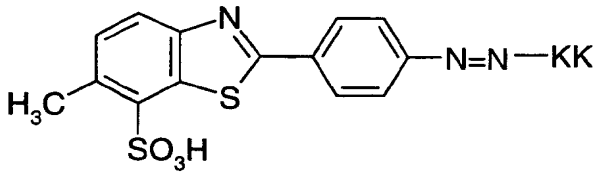
g) optionally dissolving the anionic organic compound by addition of a suitable base.

2. A process according to claim 1, wherein a dye, a fluorescent whitening agent or an intermediate for the preparation thereof is used as the anionic organic compound.

3. A process according to claim 2, wherein a dye containing at least one sulfonic acid group and/or carboxylic acid group from the following classes of dyes is used: metal-free or metal-containing mono-, bis- and poly-azo dyes, pyrazolone, thioxanthone, oxazine, stilbene, formazan, anthraquinone, nitro, methine, triphenylmethane, xanthone, naphthazarine, styryl, azastyryl, naphthoperinone, quinophthalone and phthalocyanine dyes.

4. A process according to claim 3, wherein an azo dye containing at least one sulfo group, especially a so-called azo direct dye referred to in The Colour Index, Third Edition, Volume 2 (The Society of Dyers and Colourists, 1971), is used.

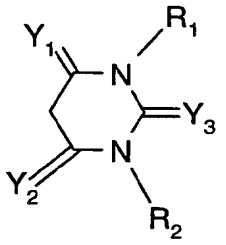
5. A process according to claim 4, wherein a dye of formula



(1),

wherein KK is the radical of a coupling component,
is used.

6. A process according to claim 5, wherein a dye of formula (1), wherein KK is a coupling component of formula



(2),

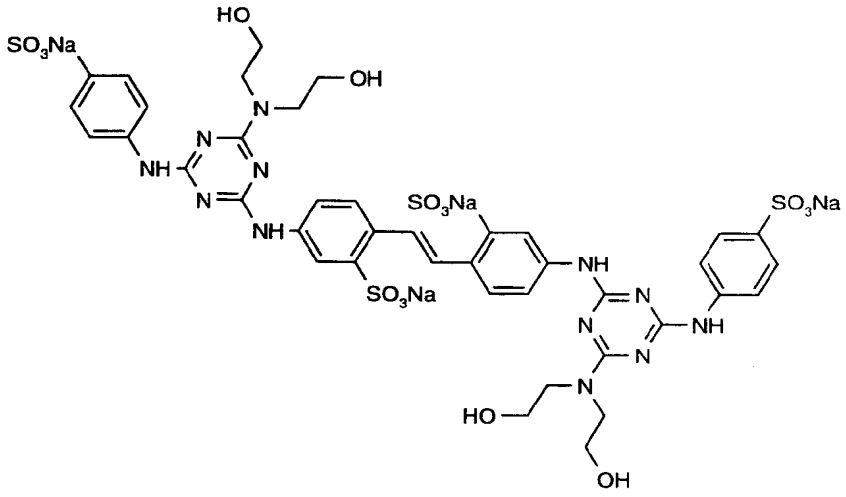
wherein
Y_1 and Y_2 are each independently of the other =O, =NH or =N-C_1-C_4alkyl,
Y_3 is =O, =S, =NR or =N-CN, R being hydrogen or C_1-C_4alkyl, and
R_1 and R_2 are each independently of the other hydrogen, unsubstituted or substituted alkyl or unsubstituted or substituted phenyl,
is used.

7. A process according to claim 6, wherein a dye of formula (1), wherein KK is a coupling component of formula (2), wherein R_1 and R_2 are hydrogen or C_1-C_4alkyl,
Y_1 and Y_2 are =O or =NH and
Y_3 is =O, =S, =NH or =N-CN,
is used.

8. A process according to claim 1, wherein the dye Direct Yellow 11, Direct Yellow 6 or Direct Orange 15 is used.

9. A process according to claim 2, wherein a sulfo- and/or carboxy-group-containing fluorescent whitening agent from one of the following classes is used: bis(triazinylamino)-stilbenes, bis(triazolyl)stilbenes, bis(styryl)biphenyls and bis(benzofuranyl)biphenyls, bis(benzoxalyl) derivatives, bis(benzimidazolyl) derivatives, coumarin derivatives and pyrazoline derivatives.

10. A process according to claim 9, wherein the fluorescent whitening agent



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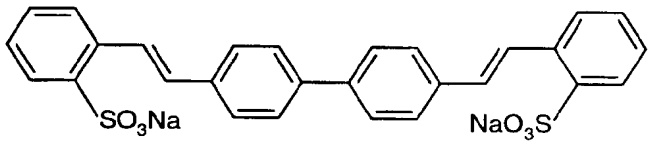

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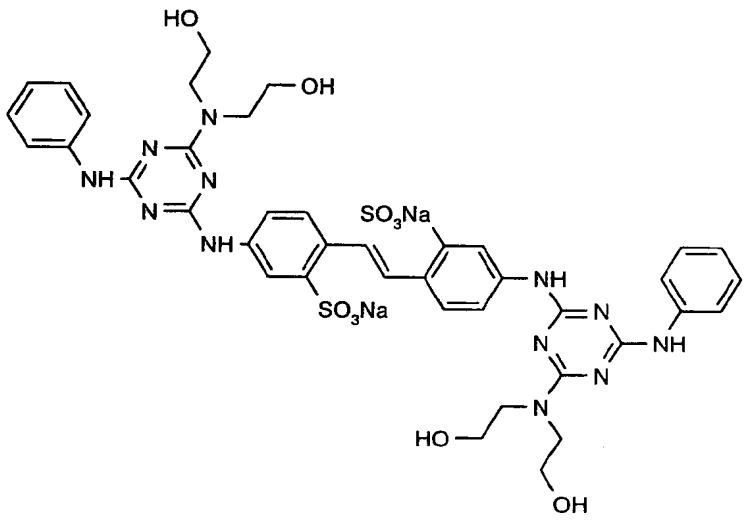

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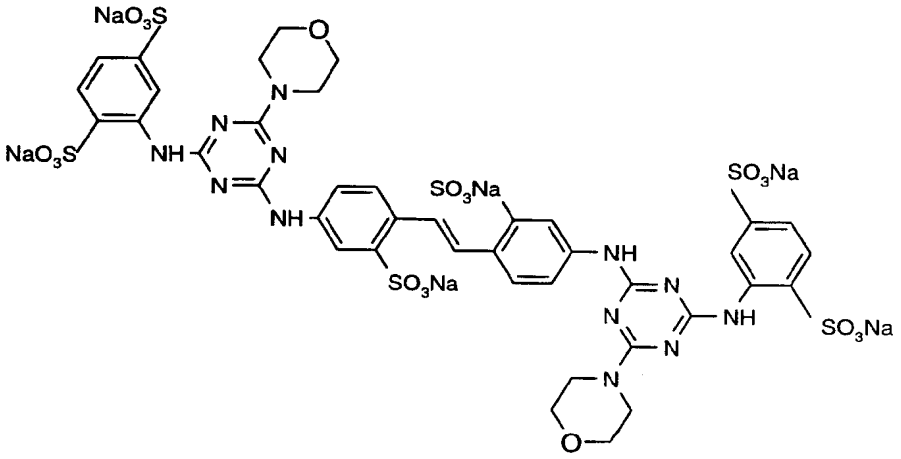
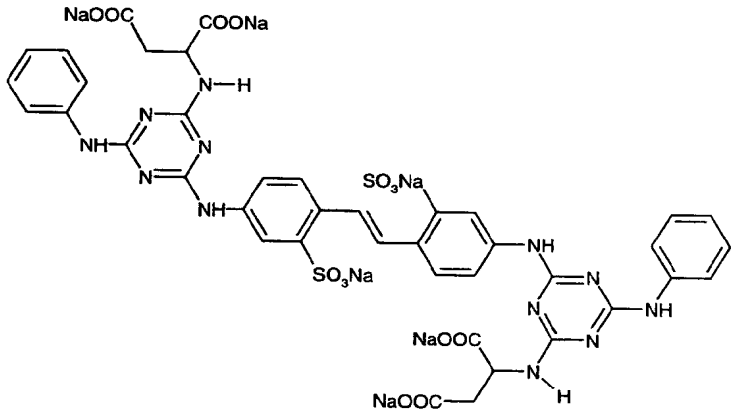


(6)

or



(7)

is used.

11. A process according to claim 2, wherein an aromatic sulfonic acid that also carries one or more further substituents from the series amino, nitro, alkyl and hydroxy is used as the anionic intermediate.

12. A process according to claim 11, wherein 2-amino-5-hydroxynaphthalene-7-sulfonic acid, 4-aminotoluene-2-sulfonic acid, dehydroparathiotoluidinesulfonic acid, 4,4'-diaminostilbene-2,2'-disulfonic acid, 4,4'-dinitrostilbene-2,2'-disulfonic acid, 4,4'-diamino-diphenylamine-2-sulfonic acid or 4-nitrotoluene-2-sulfonic acid is used.

13. A process according to any one of claims 1 to 12, which comprises starting from an aqueous synthesis solution or suspension that, besides the anionic organic compound, also comprises greater or lesser amounts of starting materials, secondary products, salts or other impurities.

14. A process according to claim 13, wherein particular or all sulfo or carboxy groups in the salt of the anionic organic compound in the synthesis solution or suspension are first converted into the free acid.

15. A process according to any one of claims 1 to 14, wherein the microfiltration is carried out using a ceramic membrane or an acid-resistant organic membrane having a pore size of from 20 to 1000 nm, especially from 100 to 800 nm.

16. A process according to any one of claims 1 to 14, wherein the ultrafiltration is carried out using a ceramic membrane or an acid-resistant organic membrane having a pore size of from 1 to 20 nm.

17. A process according to any one of claims 1 to 16, wherein the micro- or ultra-filtration is carried out at from room temperature to about 95°C, preferably from 50 to 85°C.

18. A process according to any one of claims 1 to 17, wherein the micro- or ultra-filtration is carried out at a pressure of from 1.5 to 10 bar, preferably from 3 to 6 bar.

19. A process according to any one of claims 1 to 18, wherein the micro- or ultra-filtration is so carried out that a content of inorganic salts of less than 2 % by weight, preferably less than 0.5 % by weight, based on the total weight of the suspension, is obtained.

20. A process according to any one of claims 1 to 19, wherein the micro- or ultra-filtration is so carried out that a content of anionic organic compound of from 5 to 50 % by weight, especially from 10 to 40 % by weight, based on the total weight of the suspension, is obtained.

21. A process according to any one of claims 1 to 20, wherein, after the micro- or ultra-filtration, LiOH, NH_4OH or an organic amine is added to the low-salt or salt-free suspension obtained.

22. A process according to claim 21, wherein a C_4-C_{12}trialkylamine, C_4-C_{12}dialkylamine, C_2-C_{15}alkanolamine or polyglycol amine is used as the organic amine.

23. A solution, obtained by the process according to any one of claims 1 to 22, of an anionic organic compound.

24. The use of a solution according to claim 23 for dyeing or whitening paper or for the synthesis of an anionic organic compound.

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/EP 00/10415

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09B67/54

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 652 044 A (BAYER) 10 May 1995 (1995-05-10) page 3, line 52 -page 4, line 5	1-22
X	examples page 5, line 24 - line 46 page 2, line 24 -page 3, line 17	23
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X	page 6, paragraph 2 - paragraph 4; examples	23
A	DE 33 01 870 A (BAYER AG) 26 July 1984 (1984-07-26) page 4, line 22 -page 7, line 15; example 3	1-24

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
9 February 2001	19/02/2001

Name and mailing address of the ISA	Authorized officer
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INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/EP 00/10415

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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A	EP 0 049 802 A (BAYER) 21 April 1982 (1982-04-21) page 7, line 12 -page 8, line 7 page 9, line 1 - line 10 page 9, line 18 -page 10, line 7 page 10, line 17 -page 11, line 3	1-24
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